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PATTERNED ELECTROSPRAY FIBER STRUCTURES

by
Phillip Gibson
and
Heidi Schreuder-Gibson

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14. ABSTRACT

Electrospun fibers have useful filtration properties for chemical protective clothing and filter masks. Techniques for the patterned deposition of these fibers have been developed based on varying the conductivity of the target substrate. We are investigating multilayer arrangements of patterned fibers deposited in single layers, and onto air-permeable substrates. Patterning through the depth and across the area of the deposited layers has an effect on membrane strength. These materials are possible add-on solutions to provide complete biological and chemical aerosol particle protection for air permeable garments. Enhanced filtration efficiency of woven and nonwoven fabrics will improve individual soldier protection without compromising air flow characteristics or comfort of air-permeable garments.

15. SUBJECT TERMS

FIBERS	MEMBRANES	MULTILAYERS	ELECTROSPINNING
FABRICS	FILTRATION	PERMEABILITY	ELASTIC PROPERTIES
AEROSOLS	NANOFIBERS	ELECTROSTATICS	PROTECTIVE CLOTHING
CLOTHING	PENETRATION	AIR PERMEABILITY	

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Preface and Acknowledgements

This reports documents research on elastic electrospun membranes performed by the Natick Soldier Center, U.S. Army Research, Development and Engineering Command, under project number BR 20028, funded by the Department of Defense Chemical and Biological Defense Science and Technology Program, during the period January 2003 to January 2005.

The authors are grateful to Ms. Nalini Gupta for preparing some of the intricately patterned electrospun membranes while working at Natick as an MIT summer student intern.

PATTERNED ELECTROSPRAY FIBER STRUCTURES

1. Introduction

Electrospinning is a process for making extremely fine submicron fiber by a process of charging polymer solutions to thousands of volts. This method of manufacturing man-made fibers has been known since 1934, when Formhals filed the first patent on electrospinning [1]. Electrospinning occurs when a polymer solution or melt is charged to high voltage to produce fibers. Voltages of 5kV to 30kV are sufficient to overcome surface tension forces of the polymer, and a free surface of charged polymer will produce fine jets of liquid that are rapidly drawn toward a grounded target. The jet splits a few times near the liquid surface, but before it reaches the target, substantial drawing is observed in a series of looping actions of the rapidly solidifying fiber [2]. The fiber is often collected as an interconnected web of small filaments on the surface of a grounded target.

Despite the long history of electrospinning technology, it has never been applied to fabrics as a protective membrane layer. This new application has been under development at the U.S. Army Natick Soldier Center for the purpose of providing protection from extreme weather conditions, enhancing fabric breathability, increasing wind resistance, and improving the chemical resistance of clothing to toxic chemical exposure. Due to the fine fiber size and large expected surface area, electrospun membranes possess the features desirable for catalyst immobilization substrates, absorbent media and encapsulated active ingredients, such as activated carbon and various biocides.

2. Background

The current work is similar to previous studies we have carried out for nanofiber coating on open-cell polyurethane foam loaded with activated carbon particles [3]. Nanofiber spray coatings were applied directly to the foam, and aerosol particle filtration and air flow properties were measured as a function of deposition thickness. The difference in the present work is the use of different substrates, and intentional gradient patterning of the spray. Examples of this past work are shown in Figures 1 and 2.

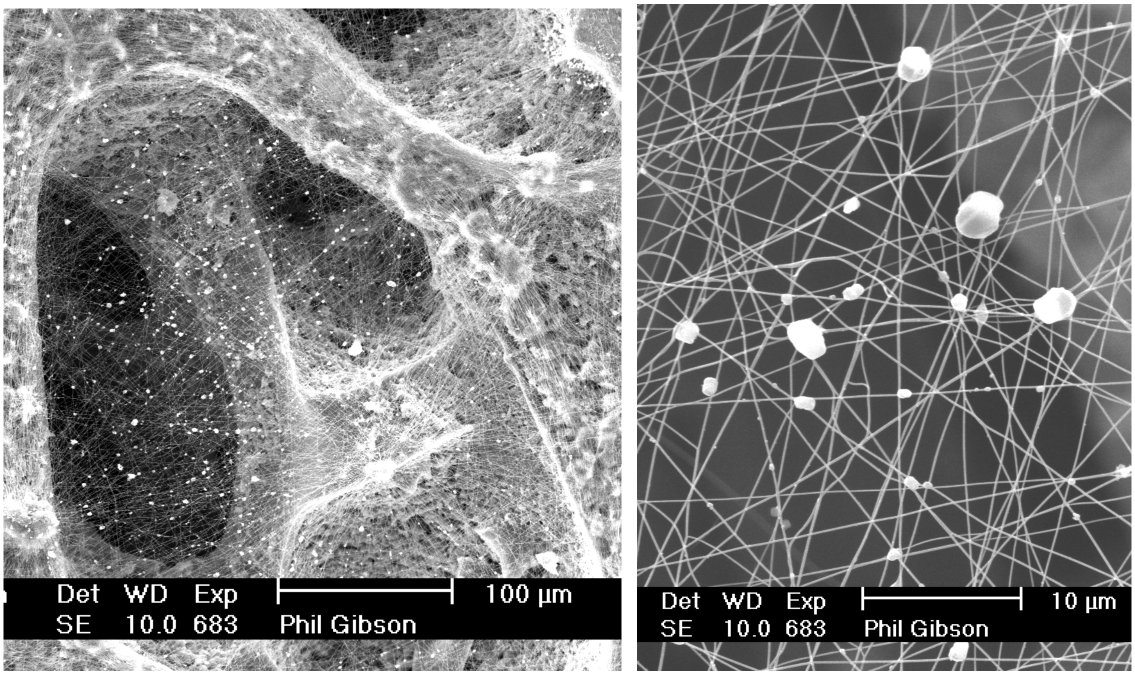


Figure 1. Aerosol particles (small white particles) captured in nanofiber web covering large pores in activated carbon loaded polyurethane foam.

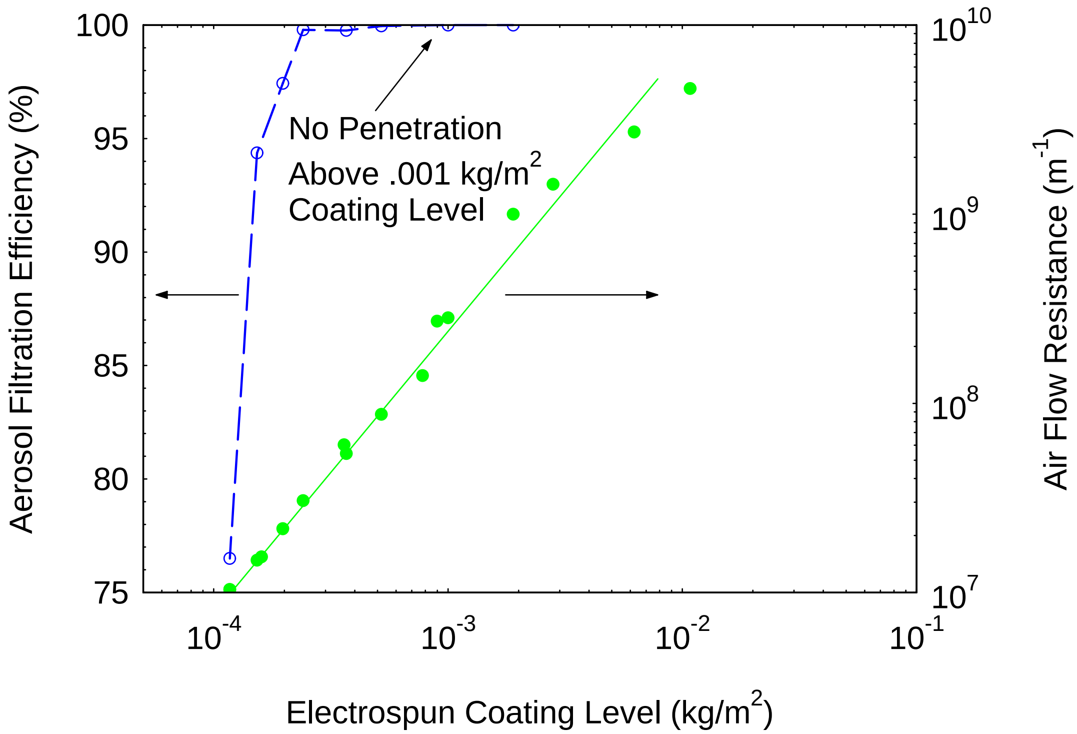
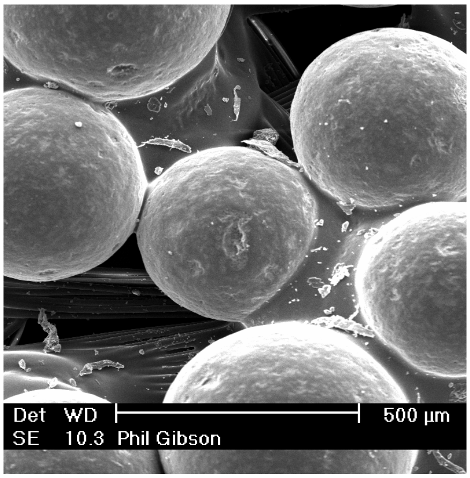
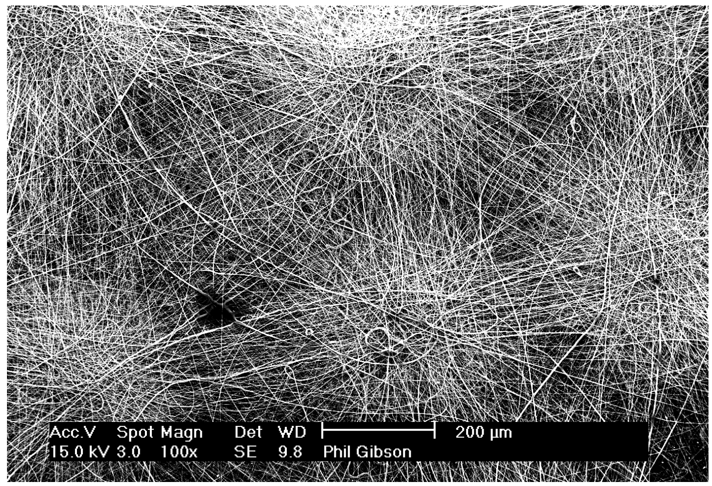


Figure 2. Aerosol particle filtration efficiency and air flow properties of electrospun nanofiber coating applied directly to sorptive carbon foam [3].

An objective of this work is to produce the patterned electrospun fiber layer applied directly to other substrate materials. A good example of patterning is found when fibers are electrospun directly onto an activated carbon sphere filter fabric used in military chemical protective garments. The activated carbon spheres are fairly conductive and provide a good patterning target for the charged fibers. Figure 3 shows the natural patterning when spinning directly onto the carbon spheres.



Activated carbon spheres



Electrospun fibers coated onto spheres

Figure 3. Example of patterning on carbon bead array due to higher electric conductivity of activated carbon spheres.

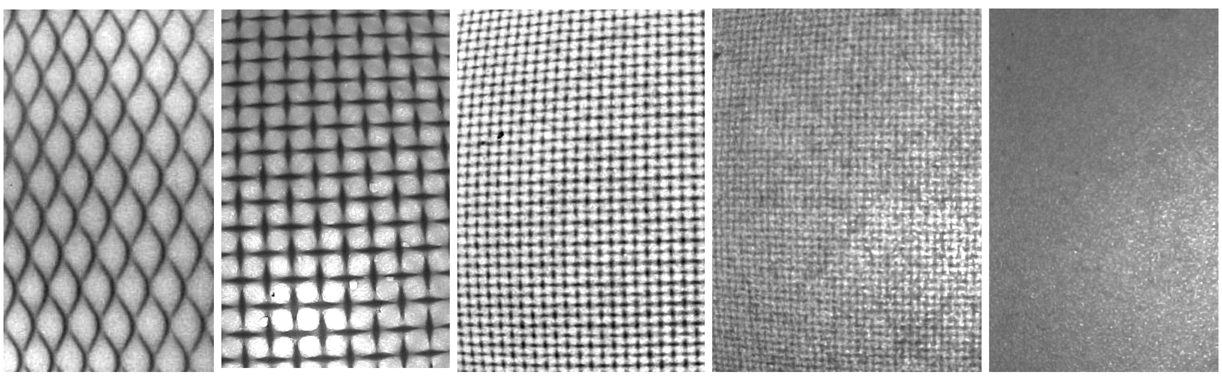
3. Approach

The challenge in this current work is to develop a density gradient through the coating thickness, as well as intermingling fibers of different compositions together into the web. A conductive patterned substrate is put behind the target textile, and the pattern can be varied by shifting during the electrospray process to produce the desired gradients through the thickness and across the surface. Deposition density can be controlled by lateral shifting as well as by changing the separation between the conductive pattern and the back of the textile spray target. Shifting of the pattern during the fiber spray deposition will also increase the tortuosity of the interconnected pores formed by the fiber bed. Increase in tortuosity should result in higher filtration efficiency for a given thickness. Patterning may also be a viable way to increase the stand-alone strength of an electrospun membrane. A pattern similar to that seen on the surface of a ripstop fabric is formed with a square grid pattern. The thicker pattern laid down on the more conductive grid results in higher mechanical strength, while filtration and air permeability are maintained in the thinner regions between the reinforced areas.

Methods for controlling electrospun fiber patterning have been developed by several groups. Bunyan et al. [4] were able to control fiber deposition patterns by controlling electrode and target configuration. White and coworkers [5] developed several electrospun fiber patterning techniques for "gossamer space structures (solar sails based on Mylar films)" and adhesive layers coated onto textiles. Yarin and coworkers [6,7] showed how to produce aligned fibers and nanofiber structures by manipulating electric fields and targets.

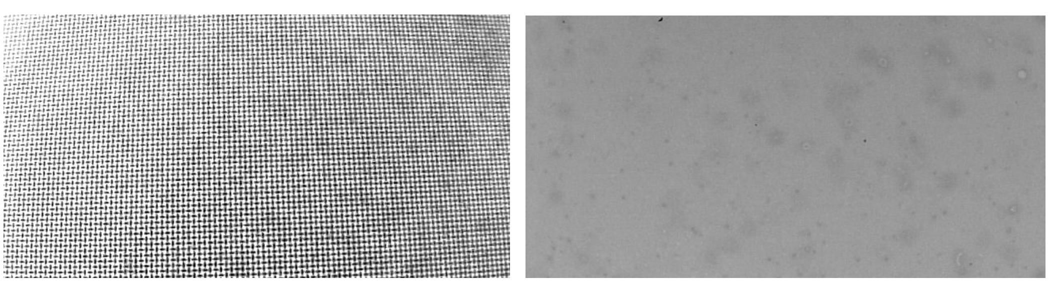
We are building upon these techniques to electrospin directly onto various conductive targets to produce stand-alone fibrous membranes. We are concentrating on three polymers at present. Two of these are elastomeric thermoplastic polyurethanes: Estane from Noveon/B.F. Goodrich, designated as TPU-1, and Pellethane from Dow Chemical, designated as TPU-2. These polymers are tough, highly elastic, have good stress recovery, and are fairly easy to spin. The other polymer is Nylon 6. Nylon produces fibers about 10 times smaller than TPU-1 and TPU-2 (100 nm versus 1 μm), but is not elastic, and tends to be brittle and papery in thick applications. We are using nylon because it provides very precise targeting of patterns, and will help us determine the limits of resolution of patterning and offsets. The thermoplastic polyurethanes also pattern well, but because of the larger fiber size will not provide the resolution of patterning possible with nylon.

We produced electrospun patterned grids with TPU-1, TPU-2, and Nylon 6. Conductive patterns include metal screens, perforated metal grids, and cotton fabrics that are wetted to enhance their conductivity. Electrospun membranes produced with the screens are shown in Figs 4 and 5.



Coarse grids (0.21 and 0.13 cm spacing) | Medium grid (0.044 cm spacing) | Fine grid (0.026 cm spacing) | No grid

Figure 4. Examples of electrostatic patterning using various conductive grids with TPU-1 (thermoplastic elastic polyurethane). Electrospun membrane removed from conductive grid and photographed with back light. Scale - each picture is about 2 cm across. An additional very fine grid with spacing of 0.0078 cm is not shown here.



Fine grid (0.026 cm spacing) | No grid

Figure 5. Example of electrostatic patterning for Nylon 6. Nylon spun at 15 kV from formic acid. Scale - each picture is about 2 cm across.

Patterns can be produced by spinning directly onto a conductive grid, or onto a grid placed beneath a nonconductive substrate. Different patterns through the depth of the membrane layer may be produced by shifting the conductive grid during the spinning process. Figure 6 shows the results of rotating and translating the underlying conductive grid.

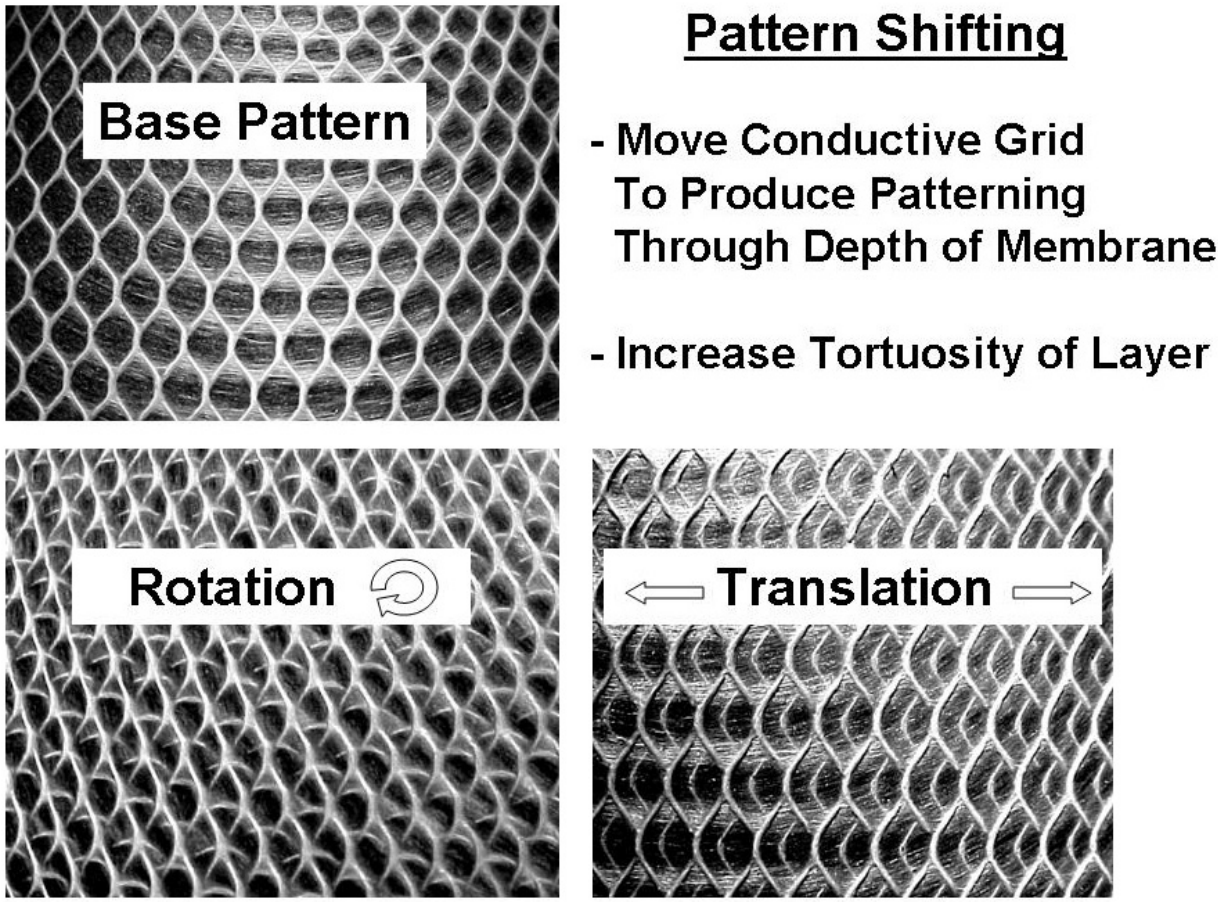
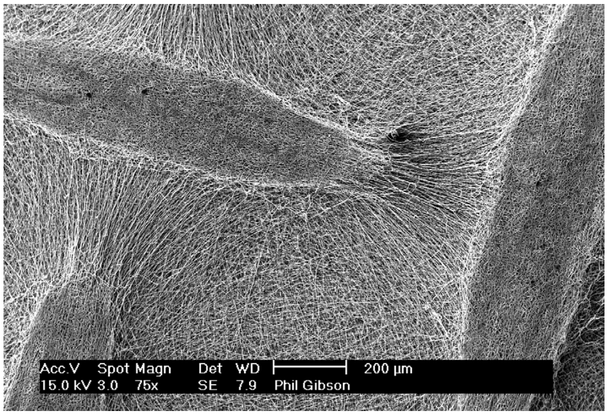
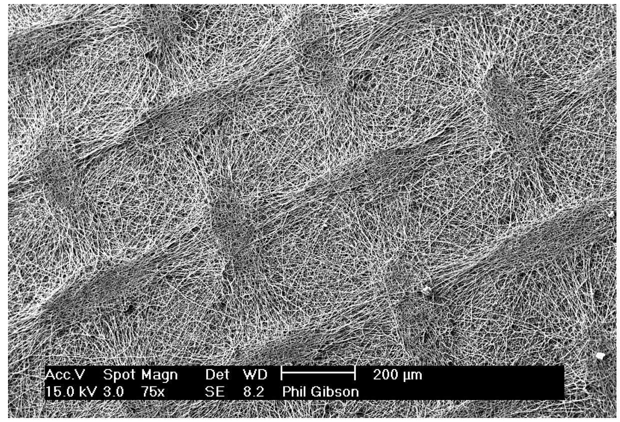


Figure 6. Patterning through the depth of an electrospun membrane by produced by shifting the underlying conductive grid pattern during fiber deposition.

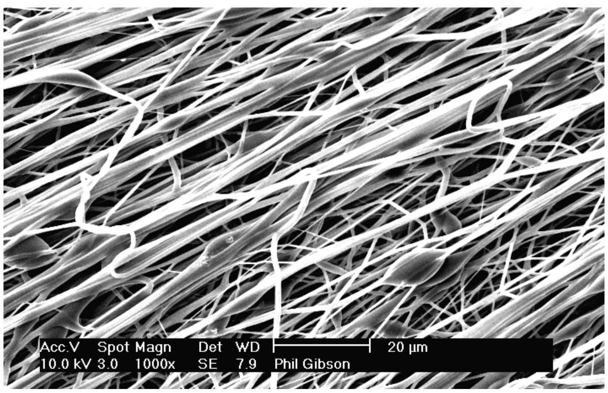
Figure 7 shows the fiber deposition pattern resulting from spinning directly onto a conductive wire grid. The charged fibers are preferentially attracted to the metal wires, and are often oriented parallel to the wire axis. Figure 8 shows that the smallest electrospun polyurethane fibers are generally larger in size than those produced from Nylon 6 (500 nm versus 100 nm fiber diameter).



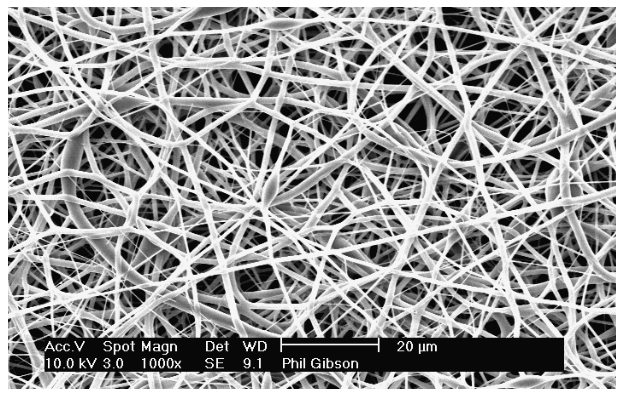
Coarse grid



Medium grid

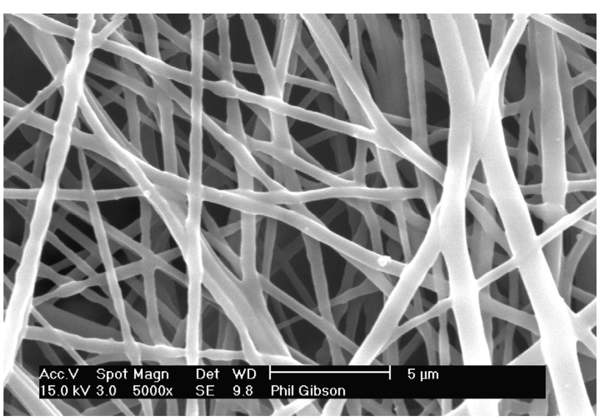


Aligned fiber region over conductive substrate

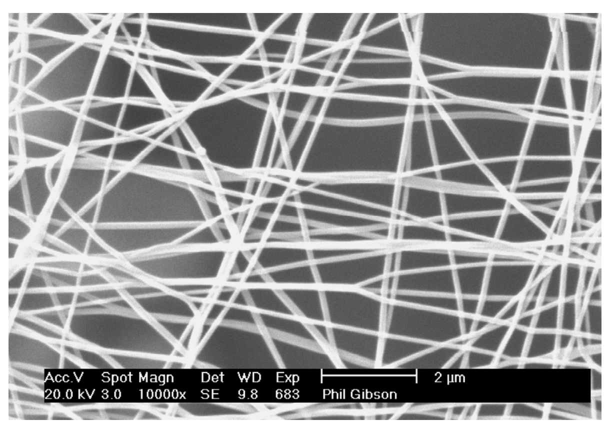


Random fiber orientation away from conductive substrate

Figure 7. Alignment of electrospun fibers over conductive substrate.



Electrospun TPU-1 (5000x)



Electrospun Nylon (10,000x)

Figure 8. Relative fiber sizes for TPU-1 (0.5-3 µm) and Nylon (0.1-0.5 µm).

One of the advantages of the polyurethane membrane is that it is highly elastic, tough, and can stretch along with other materials it may be attached to. A demonstration of the elastic behavior of a stand-alone electrospun polyurethane membrane is shown in Figures 9 and 10. The ability to stretch under pressure is particularly important in clothing applications. A stretchable membrane may have other applications such as self-cleaning in reverse flow. In the intake phase the membrane filters out particles, and experiences minimum deflection if it is against a support backing. In the exhaust phase the membrane expands like a balloon under the pressure of the airflow, the pores open up much wider, aerosol particles are released, and the pores are unclogged.

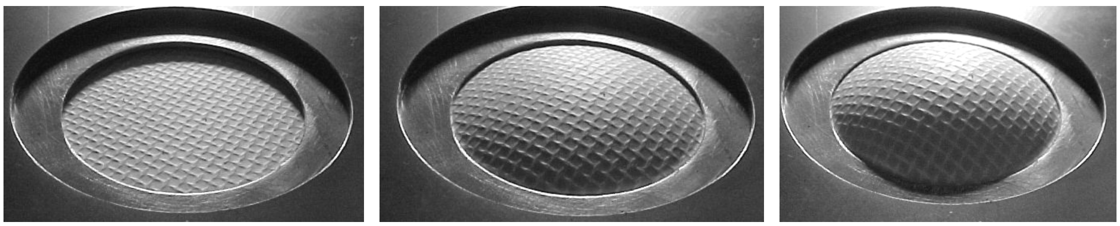
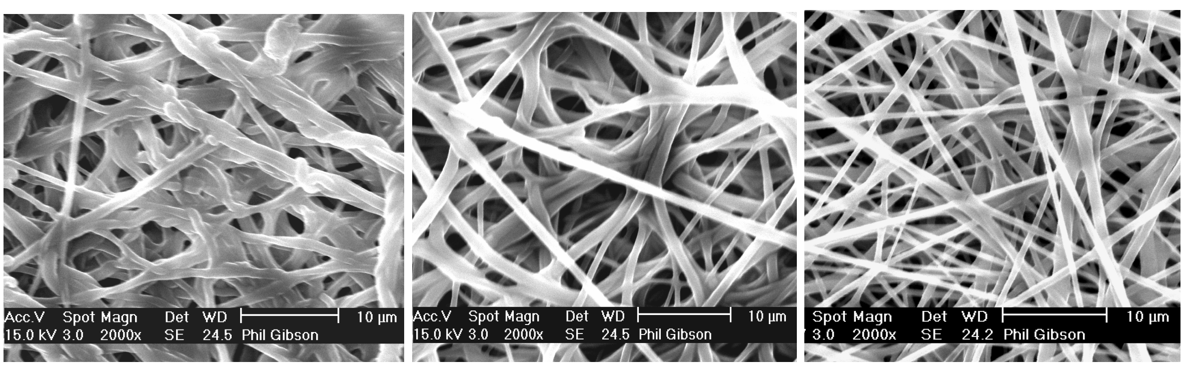


Figure 9. Illustration of elastic behavior of patterned membrane. Membrane pressurized with gas from below. Electrospun elastomeric polyurethane, large grid pattern.



0% strain 50% strain 100% strain

Figure 10. Elastic behavior of electrospun thermoplastic polyurethane under biaxial elastic strain.

4. Results

Pore Size and Air Flow Resistance

Electrospun fibrous membranes are porous materials. The porosity, pore structure, and pore size determine most of the transport properties we are interested in for these materials (such as air flow resistance and particle filtration). The electrospun porous membranes we make usually have porosities in the range of 60% to 80%, which is comparable to normal nonwoven and woven textiles. The two main variables controlling the transport properties of these membranes are thickness and fiber size. Fiber size is directly related to apparent pore size (the spaces in between the fibers). Thickness is controlled by coating time or deposition rate, while fiber size is influenced by a variety of processing variables including fluid conductivity, fluid viscosity, fluid surface tension, charge density, target distance, and field strength [8-11].

Pore size and air flow resistance were measured with a liquid capillary expulsion porometer [12]. Smaller mean fiber diameters create smaller mean pore sizes in the electrospun membrane porous structure. Porometry provides a good indication of fiber diameter since the mean pore size is usually of the same magnitude as the mean fiber size. Typical values of air flow resistance and mean pore sizes for electrospun membranes, microfiber fabrics, textiles, and nonwovens are shown in Figure 11. Note that air flow resistance (m^{-1}) is essentially the inverse of the more familiar units of air permeability ($ft^3/min/ft^2$) as used in the textile industry.
Air flow resistance (R) is defined by R (1/m) = $\Delta pA/Q\mu$, where: Δp = pressure drop (N/m^2); A = sample flow area (m^2); Q = volumetric flow rate (m^3/s) ; μ = air viscosity (17.85×10^{-6} kg/m-s at 20°C).

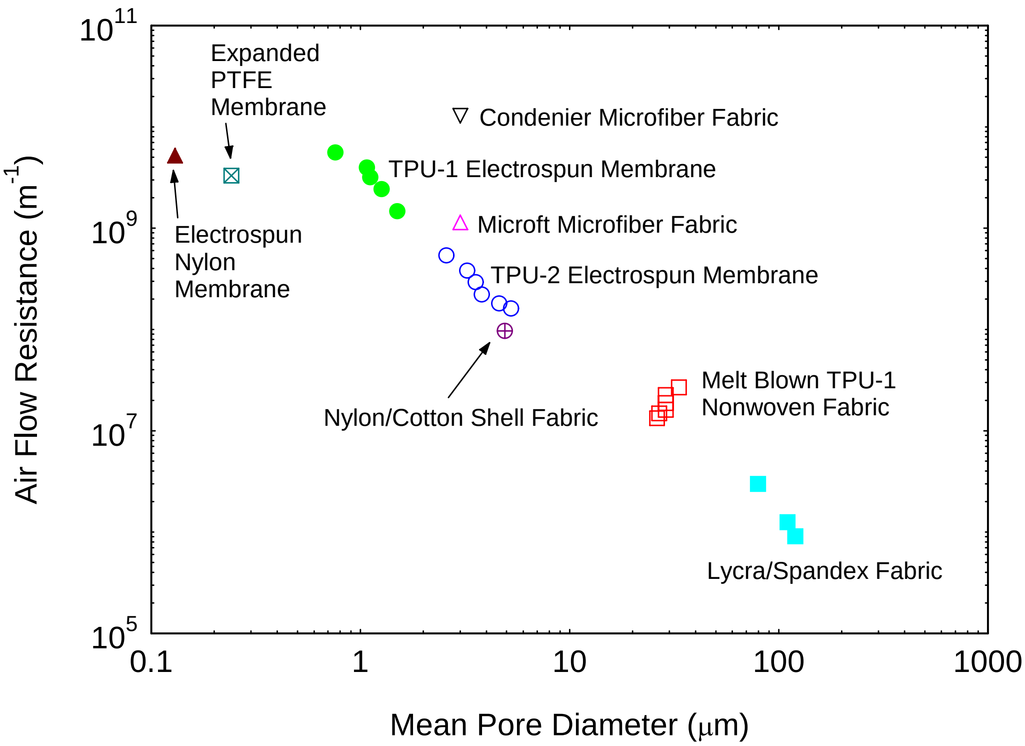


Figure 11. Typical pore sizes for electrospun membranes, fabrics, and nonwovens.

We used porometry to see if patterning affects the mean pore size and air flow resistance of the electrospun membranes. We found that there was no obvious effect of patterning on either mean pore size or air flow resistance of the stand-alone electrospun elastic membranes (Figures 12 and 13). The differences between patterned samples seem due more to random scatter than to any factors having to do with the grid spacing of the patterned samples.

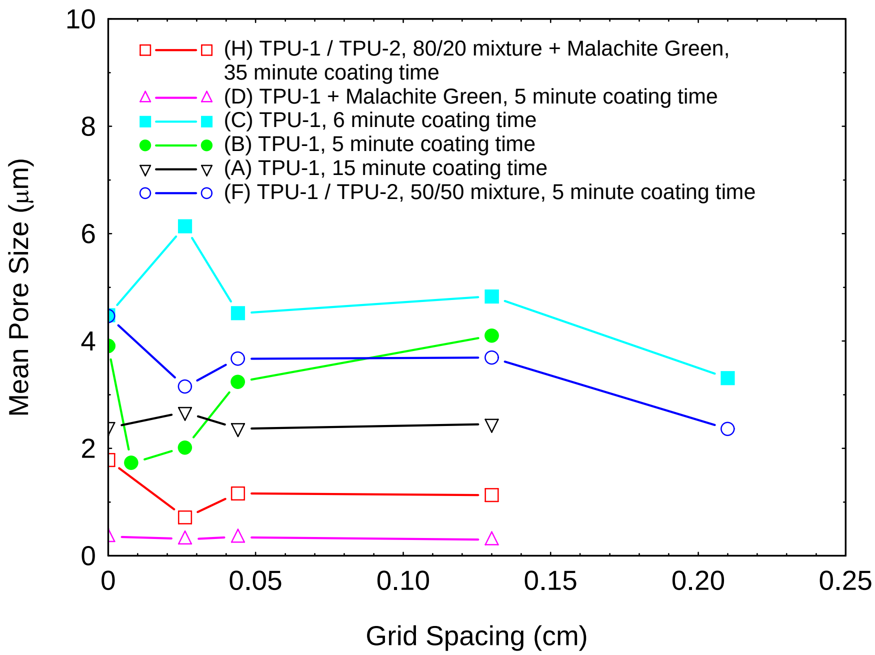


Figure 12. Patterning and grid spacing has no clear effect on mean pore size of electrospun elastic membranes.

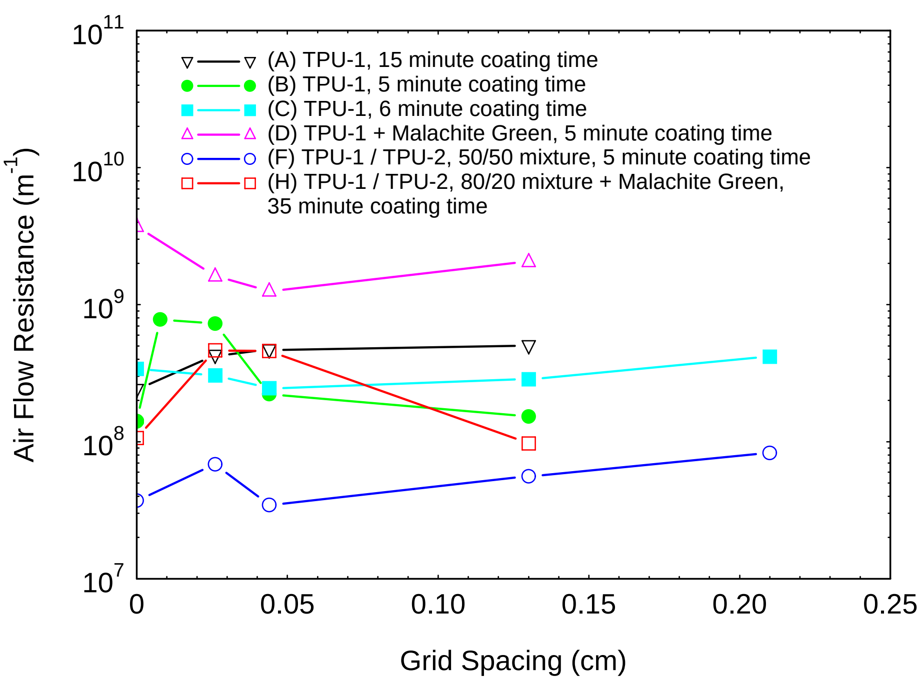
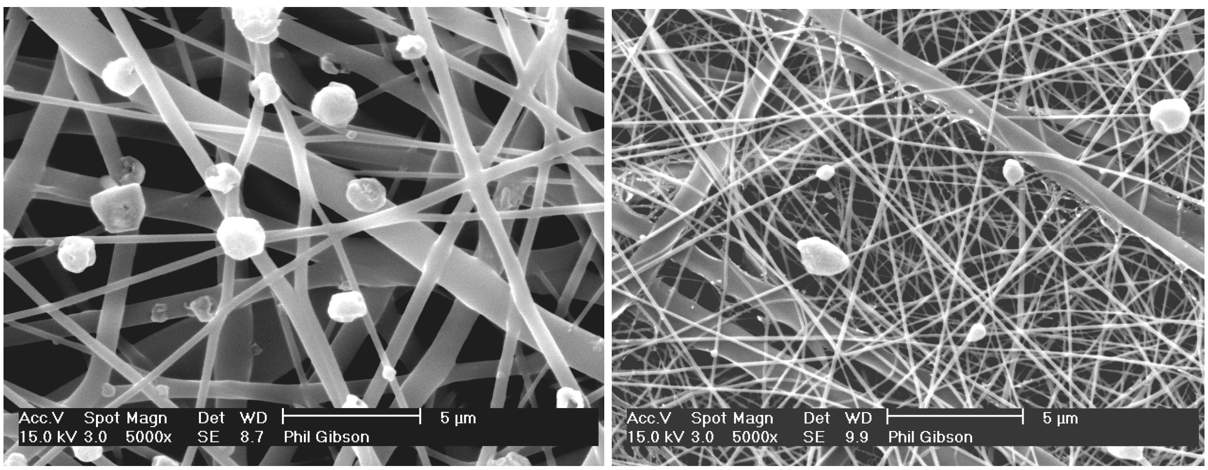


Figure 13. Patterning and grid spacing has no clear effect on air flow resistance of electrospun elastic membranes.

Aerosol Particle Filtration

Electrospun fibers are effective filtration media, and are produced commercially for various types of filter products [13]. As mentioned previously, we have been exploring electrospinning as a way to enhance the filtration efficiency of existing clothing materials, particularly by using elastomeric polymers that are able to stretch with and conform to the base fabric without suffering damage.

The patterned electrospun samples were tested for aerosol particle filtration using potassium iodide particles with a mean geometric diameter of 1.8 µm and a fairly narrow distribution between 1 and 3 µm. Further details on the aerosol filtration test system are available in Reference 14. Figure 14 shows the relative sizes of the potassium iodide test aerosol and the fiber sizes in the electrospun membrane samples.



TPU-1 Nylon 6

Figure 14. Potassium iodide test aerosol particle capture in electrospun TPU-1 and electrospun Nylon 6.

In this phase of the work we are producing fairly thick stand-alone membranes, and nearly all the materials tested were able to completely filter out the test aerosol. However, we would expect that we would see some penetration of aerosols through the electrospun fiber layer when the electrospun fibers are coated in very thin layers onto other substrates, which has been our experience in the past [15]. Since we saw no effect of the fiber patterning on the measured pore size or air permeability, we would also expect to see little effect of patterning on aerosol particle filtration properties. Future work calls for aerosol testing of thin patterned layers sprayed onto woven and nonwoven textile substrates, and we expect to see some aerosol penetration for the very thinnest electrospun layers on such materials.

Figure 15 shows aerosol particle penetration for three patterned materials. Two of the materials are a thin layer of electrospun TPU-1 (5 minute coating time) and a mixture of electrospun TPU-1/ TPU-2, also coated for 5 minutes. This coating was thin enough to allow some particle penetration. The third material is a much thicker electrospun layer of TPU-1/ TPU-2 (35 minute coating time) that allowed very little aerosol particle penetration.

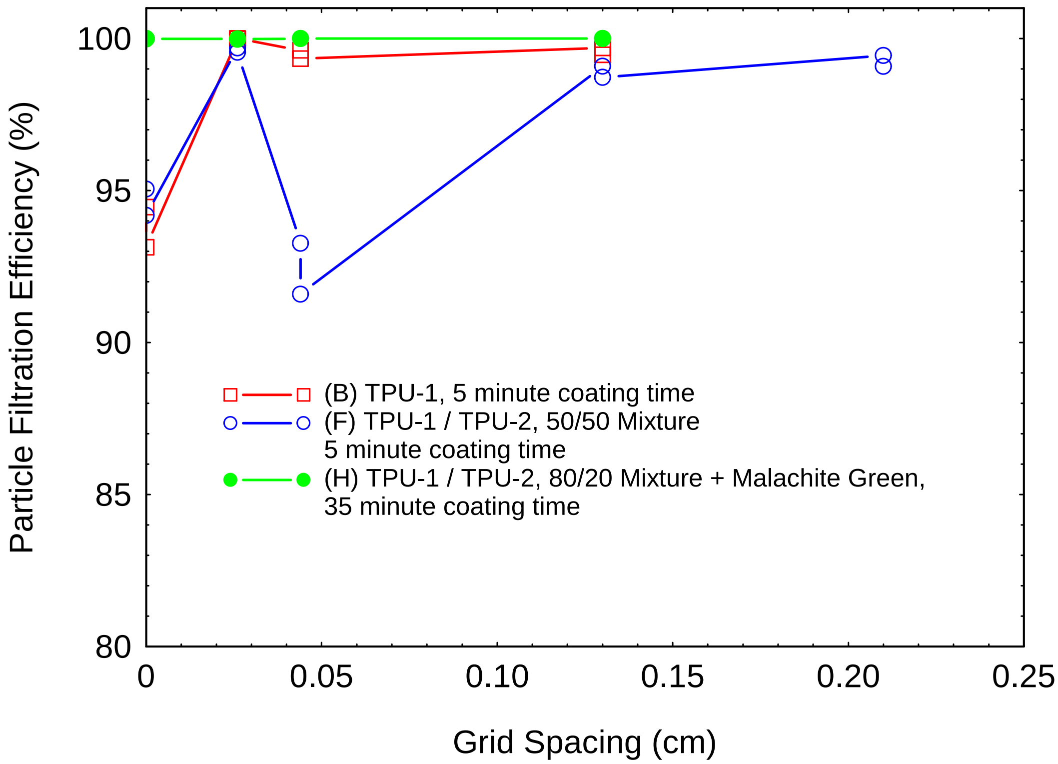


Figure 15. Patterning has no clear effect on aerosol filtration properties of elastic electrospun membranes.

One of the reasons we are interested in the patterned electrospun layers is the ability to produce nonuniform densities across the area and through the thickness of the sample. We hope to increase the filtration efficiency of an electrospun layer by forcing air and particles to follow a more tortuous path through the fiber bed, thereby increasing the chance for particle capture. To achieve this, we will be varying the deposition through the thickness of the electrospun layer by shifting the conductive grid so that the high-density regions are discontinuous from one side to the other.

The test system we are using for the aerosol particle penetration measurements is not able to generate or measure particles much below 1 μm. Since the electrospun fibers are highly efficient at capturing particles of this size, it is difficult to see performance differences between different grid spacings if no particles are able to penetrate the layers. Although the pore sizes of some of these membranes are as high as 6 μm, particle diffusion and Brownian motion result in efficient particle capture in the electrospun fiber bed. Aerosol particle penetration through the very thin electrospun layers may be more dependent on small flaws and holes than in actual penetration through a uniform electrospun fiber mat thickness, as reflected in the scattered nature of the data we were able to generate. Aerosol measurements in the future will be extended to include a biological aerosol generated from MS2 virus, which has a diameter near 25 nm. This particle size will be able to more effectively penetrate the small pores of the thicker electrospun membranes, and allow us to distinguish the effects of the various grid patterns and offsets much more clearly than we are able to do with aerosol particles of 1.8 μm mean size.

Strength

Patterning may enhance the strength of electrospun layers. Fibers deposit preferentially over conductive regions, and also tend to align themselves with the underlying wire pattern. Patterning may increase the tear resistance of these membranes by the presence of thicker fiber regions that stop tears that begin in the randomly oriented areas of the membrane.

To evaluate strength properties a modified burst test was developed. This test method provided qualitative insight into the elastic capabilities of the electrospun elastomeric membranes, but needs further development to provide reproducible quantitative data.

The electrospun sample was mounted between two metal plates with circular holes. A soft rubber gasket provided sealing and protection from the metal edges of the holes. Gas pressure was slowly increased on one side of the membrane, and a pressure transducer and data acquisition system continuously recorded the gas pressure. The burst pressure is defined as the peak pressure reached before the membrane ruptures (after which the pressure falls nearly to zero).

The burst test was complicated by the fact that the electrospun layers are air permeable. As the air pressure increased, more air flowed through the material. For the elastic membranes, the pore area increased as the sample stretched, increasing the flow rate and further relieving the pressure. For some of the very air-permeable samples, it was impossible to induce rupture or tearing because the material was able to relieve the pressure by its ability to deform and increase total pore area under the imposed pressure. The usefulness of the burst test was also limited by the maximum flow rate from the gas source, and the peak pressure attainable with the data acquisition system and the pressure transducer. Burst pressures above 330 kPa (48 psi) weren't recorded, and many samples could not be pressurized to burst because they required higher flow rates than were possible with the gas delivery system used.

Figures 16-18 show typical burst test results for both a thick and a thin electrospun membrane. These particular membranes are TPU-1 thermoplastic polyurethane. The figures show that the membranes are capable of high strain without rupture. Figures 16-18 shows that the grid pattern functions effectively as a ripstop pattern in minimizing damage once the membrane ruptures and begins to tear. Figure 16 in particular shows the reinforcing effect of the coarse grid pattern on the inflated highly deformed elastic membrane.

Coarse Grid Pattern | Medium Grid Pattern | No Pattern

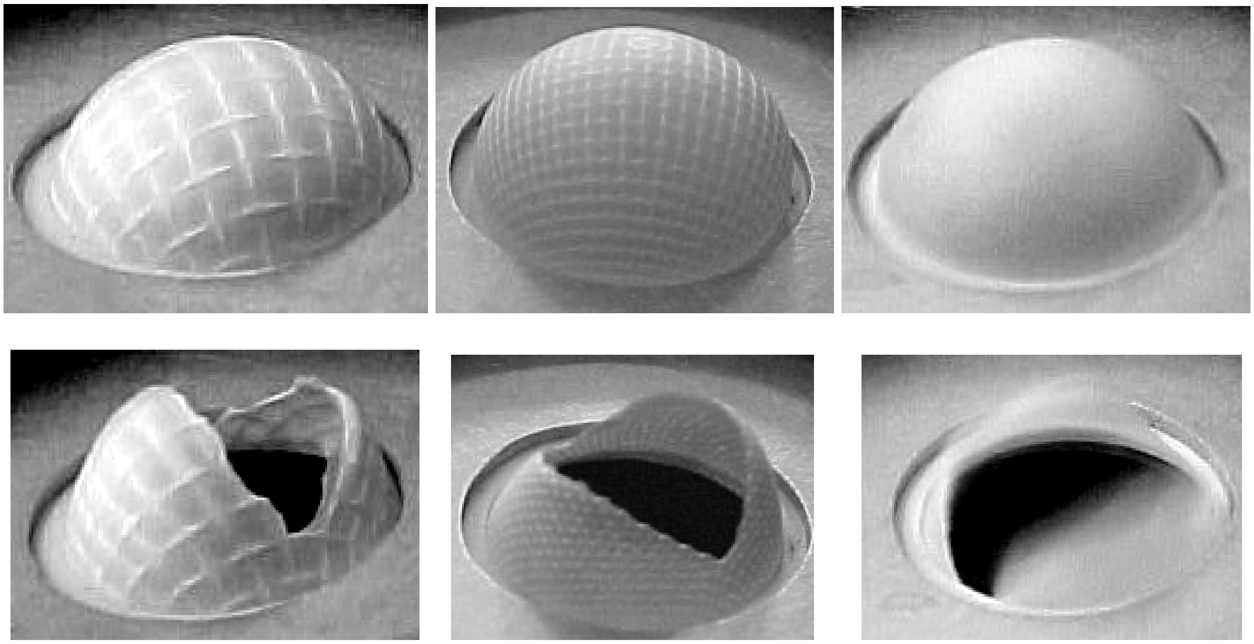


Figure 16. Burst testing of fairly thick elastomeric electrospun membranes (electrospun over 15 minute time period). Grid patterns tend to inhibit further tearing of the ruptured membrane.

Coarse Grid Pattern | Medium Grid Pattern | No Pattern

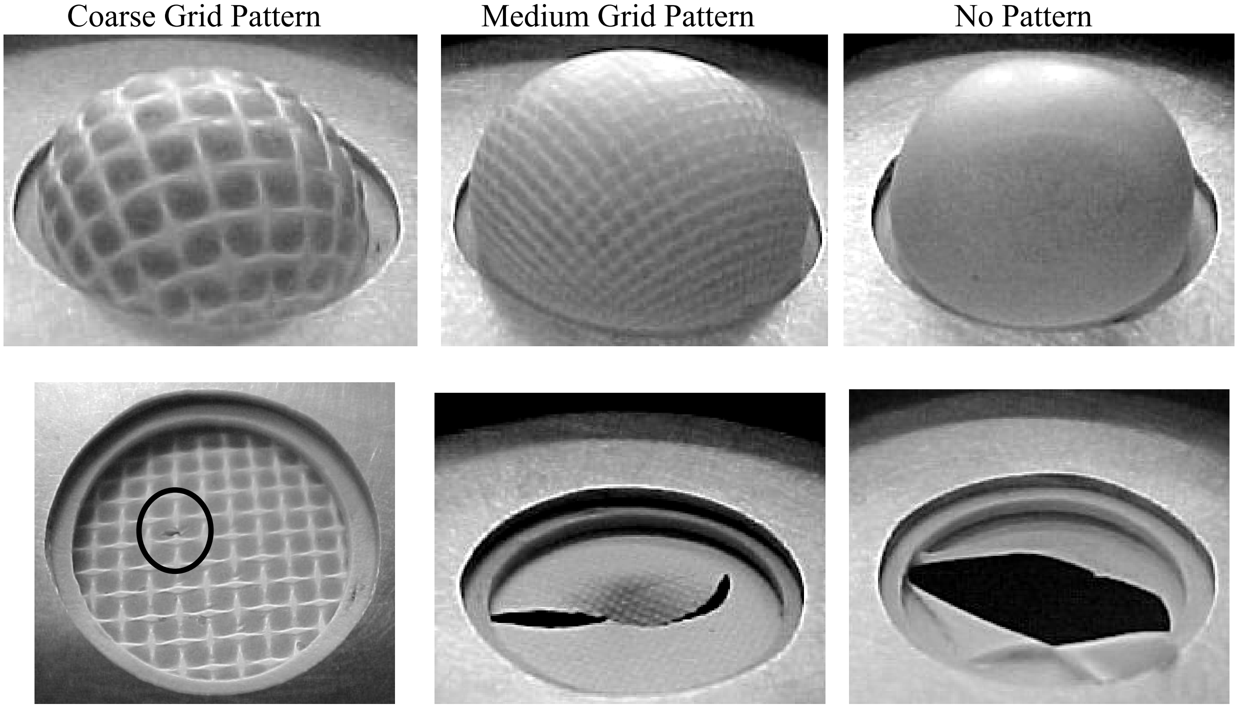
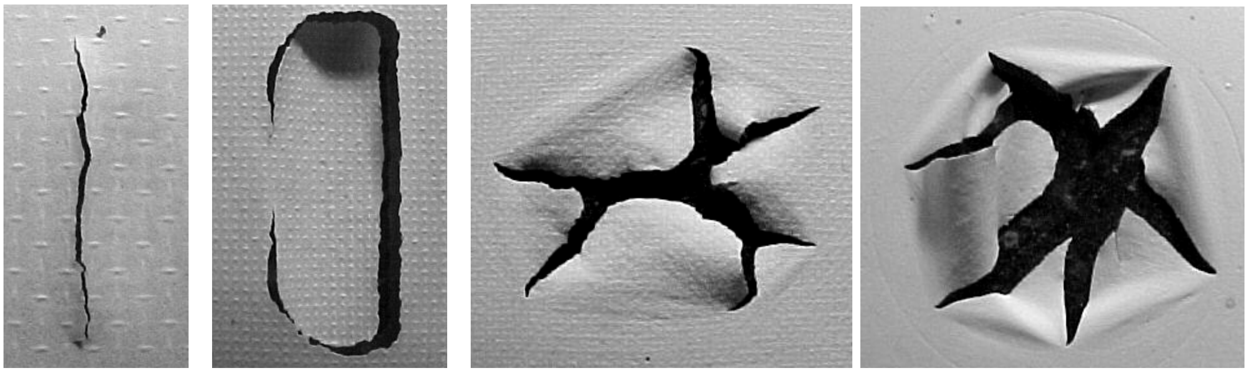


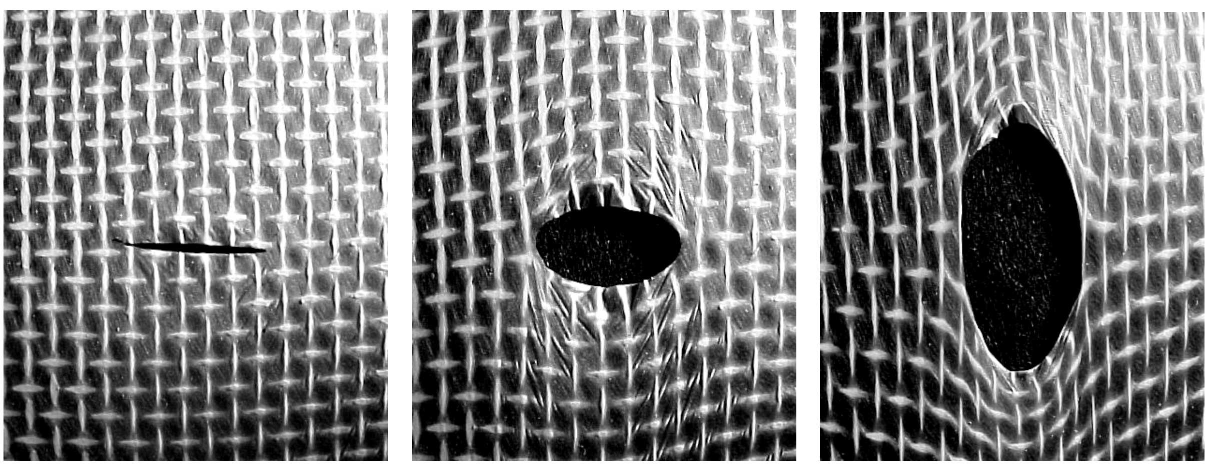
Figure 17. Burst testing of thin elastomeric electrospun membranes (electrospun over 5 minute time period). Note that grid patterns tend to inhibit further tearing of the ruptured membrane. Non-patterned sample suffered much more damage than the patterned samples. Circle on deflated coarse grid sample indicates small hole that relieved pressure without tearing.



Coarse Grid 0.13 cm spacing | Medium Grid 0.044 cm spacing | Fine Grid 0.026 cm spacing | No Grid

Figure 18. Influence of patterning on failure in burst test.

Additional strength testing is planned for these membranes. Simple uniaxial stress-strain curves or uniaxial tear strength may yield more quantifiable results than the simple burst test. An attempt at a simple tear test is shown in Figure 19. The elastomeric electrospun membranes are elastic and difficult to restrain and clamp in a tensile tear test. The deformation at the outer edges greatly influences what is happening in the damaged region. The exaggerated opening of the tear before damage begins, and the wrinkling/buckling of the membrane surface, also complicates matters. A mechanical biaxial stress/strain test method is a more appropriate test method to evaluate the tear resistance of these highly elastic patterned membranes.



Precut Crack/Tear | 20% strain | 40% strain

Figure 19. Tear testing is difficult due to elastic nature of fibers. Tear/crack begins to propagate at 40% strain. Electrospun 50% TPU-1 / 50% TPU-2 coarse grid (0.13 cm grid spacing).

The toughness and strain capability of the elastic patterned electrospun membranes is impressive. Blends of TPU-1 and TPU-2 thermoplastic polyurethanes seem to have enhanced properties and ease of electrostatic processing over either the TPU-1 or TPU-2 alone. We plan to further investigate commingling/cospinning approaches for elastomeric polymers, including materials such as butyl rubber [16].

5. Conclusions

We investigated the effect of electrostatic patterning on electrospun fibrous membranes. We found that patterning over the range of grid spacings from 0.2 cm to .008 cm produced no significant differences in mean pore size, air flow resistance, or aerosol particle filtration.

We saw qualitative differences in the failure mode and strength of patterned versus unpatterned elastomeric electrospun membranes. Pattern grid size (i.e. coarse, medium, fine) appears to affect tear propagation; patterns resist tear propagation better than unpatterned membranes. The tear resistance is enhanced by the presence of thicker regions of fibers that tend to stop tears. Since there also seems to be some fiber alignment along the metal screen wires that create the grid pattern, the membrane strength may also be enhanced through fiber orientation.

Our future plans are to extend these patterning techniques to optimize thin patterned electrospun layers coated onto other materials, such as stretchable carbon-loaded meltblown webs. We hope to enhance "tortuosity" by shifting the deposition pattern through the thickness of the electrospun layer, and to measure these changes through porometry, aerosol filtration, air flow, and diffusion measurements.

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